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THE COMPOSITION OF BIOCOMPOSITE [POLYMETHYLMETHACRYLATE/HYDROXYAPATITE] AS MATERIAL FOR SPECIMEN WITH PORTABEE KIT MACHINE

Kartinasari Ayuhikmatin Sekarjati, Alva Edy Tontowi
Department Mechanical & Industrial Engineering, Faculty of Engineering, Gadjah Mada University
Jl. Grafika No. 2, Sinduadi, Mlati, Sleman, Yogyakarta 55281
E-mail: kartinasari.sekar@gmail.com, alvaedytontowi@ugm.ac.id

Abstract *-- The development of science and technology related to bone implant material, researchers want to develop materials that have properties near human bones and improve the quality. This study was conducted to determine the composition of the mixture that can pass nozzle at room temperature. It is expected that in this study, the mixture is able to pass through the small nozzle size so that it can print specimens precisely according to the size of the design to be printed. Output mixture through a nozzle is said well if the output is continuous and homogeneous. The quality of the composition of the mixture, the material output from the nozzle will be printed by ASTM F451-95 and compressive test. This mixture consists of polymethylmethacrylate (PMMA), methylmethacrylate (MMA) and hydroxyapatite (HA) by mixing methods manually. PMMA and MMA used in the type of heat curing, while HA derived from fish scales. Through several experiments, there is composition that can pass nozzle and have a high compressive strength value, that is composition PMMA : MMA instead of 1 : 1 (w/w) with mixture 20% HA and have compressive strength value 31,20 MPa, the second composition PMMA : MMA instead of 2 : 1 (w/v) with mixture 10% HA and have compressive strength value 25,62 MPa. This composition was chosen for further research with the Portabee Kit machine.*

Keywords: *PMMA; Hydroxyapatite; Biocomposite; Bone cement.*

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INTRODUCTION

The development of science and technology related bone implant materials, researchers want to develop the material by mixing a material with other materials that have properties close to human bones. The material is also expected to improve the quality. The technology in terms of the process of printing material on a machine requires the right size of the nozzle to produce a specimen of the right size. So that it can be applied further to print human bone implant.

At present, there are various types of bone implant materials, such as allograft, autograft, bioactive glass, and bioceramics, metals, polymers, and others (Puska et al., 2011). The most widely used materials in recent years are polymethylmethacrylate or PMMA based composites (Puska et al., 2011; Zebarjad et al., 2011; Ali et al., 2015; Rashamadi et al., 2017). A mechanical property of pure PMMA is less compatible, rigid, and non-bioactive (Zebarjad et al., 2011). To improve bioactivity, PMMA-based cement is combined with inorganic substances, such as hydroxyapatite (HA) that has bioactive properties (Puska et al., 2011).

Hydroxyapatite (HA) is also often used for materials of dental implant and human bones because it has biocompatible and bioactive properties that can help the bone to grow up (Roeder et al., 2008). In this experiment hydroxyapatite (HA) is used to complement the deficiency of the properties possessed by polymethylmethacrylate (PMMA).

The compositions between materials are important to obtain high mechanical strength. The high mechanical strength is used to analyze the exact composition. This experiment will be carried out to determine the optimal composition capable of passing the nozzle. The researchers referred to a study conducted by Samad & Jafaar (2009), in which the study used PMMA powder (Mw: 120.000 and 350.000) with some powder to liquid (w/w) composition ratios of 0.75 : 1, 1 : 1, 1.25 : 1 and 1.5 : 1. The study was conducted to examine the characteristics of PMMA powder, how it was handled, and the elasticity of the PMMA sample. This research found that low powder to liquid ratio and high PMMA molecular weight can produce PMMA cement which has high flexibility and good handling.

However, commercial composition (ratio) is used for acrylic bone cement of 2 : 1 (w/v), with the provision of 40 grams powder components and 20 ml liquid components (Hosseinzadeh et al., 2013).

In the study, HA content in the biocomposite mixture did not reach 30%. Whereas the bones of living things contain a very heterogeneous composite material with the main component of hydroxyapatite (Boskey, 2013). The hydroxyapatite composition in most human bones is 70% of the mineral per dry weight. This is related to a study conducted by Zebarjad *et al.* (2011), which says that the addition of the number of hydroxyapatite (HA) may increase or decrease the mechanical strength of bone implants.

This biocomposite mixture can be formed into bone implants manually or by a 3D printing method. One type of machine that can be used is the Portabee Kit machine. The Portabee Kit machine is a 3D printing machine belonging to the Product Design and Development Laboratory of Gadjah Mada University, which initially worked with the Fused Deposition Modeling (FDM) method. This machine has undergone several modifications to previous research (Utami, 2016).

Before using the machine, it is necessary to prepare a mixture of material with the right composition. It aims to keep the mixture in the form of dough stage while still being processed on the machine and can pass the nozzle continuously. The fixed mixture in the dough stage form when processed will be removed as a whole, not harden and not clog the nozzle. Mixtures that can pass through the nozzle will continue to produce consistent output.

This study was conducted to find the composition of the mixture that can pass nozzle. To assess the quality of the composition, the material output from the nozzle will be printed and tested mechanically. The best compositions will be selected to do further research with the Portabee Kit machine.

MATERIAL AND METHOD

In this experiment, ASTM specimen F451-95 was prepared for compressive strength as shown in Fig. 1 – Fig. 8. The specimens are cylindrical with a height of 12 mm and a diameter of 6 mm as in Fig. 9.

The specimens are made of polymethylmethacrylate (PMMA) in powder form and methylmethacrylate (MMA) in liquid form, (ISO 1567 Type I Class 1, Acrylic Denture Materials), and hydroxyapatite (HA), (Bio-nano carbonate, BATAN) material from scales fish. The type of powder polymethylmethacrylate (PMMA) used in this research is heating curing because this material can pass through the 3D Printing machine. While powder polymethylmethacrylate (PMMA) type of self-curing is not able to pass through 3D Printing machine because it has a short solidification time (Utami, 2016).

Figure 1. Main Material

Equipment used in research that is:

1. Porcelain bowl, used as a place to mix material specimen forming.


Figure 2. Porcelain bowl

2. Measuring cup, used as a place of liquid material (MMA) during the burning process.


Figure 3. Measuring cup

3. Digital balance, Brand Ohaus with accuracy 0.0001 gram, used as a place to measure powder-shaped materials such as polymethylmethacrylate (PMMA) and hydroxyapatite (HA).

Figure 4. Digital balance, Brand Ohaus with accuracy 0.0001 gram

4. Plastic sample, used as a specimen that has been printed.

Figure 5. Plastic sample

5. A spatula is a spoon used in the process of measuring powder-shaped materials, and this spatula is also used to mix the specimen-forming materials on the porcelain bowl.

Figure 6. Spatula

6. The caliper with a precision of 0.02 mm is used to measure specimens that have been printed.

Figure 7. Caliper

7. The injection used as a liquid material (MMA) and this injection is used as a site for experimenting with the material mixed output via a nozzle.

Figure 8. Injection

8. ASTM F451-95 is used to print specimen.

Figure 9. ASTM F451-95

9. Mechanical strength testing machine is HT-2402 brand Hung Ta, used to test the strength of specimens that have been printed.

Figure 10. Mechanical strength testing machine

The materials are used to print specimens, such as polymethylmethacrylate (PMMA), methylmethacrylate (MMA) and hydroxyapatite (HA). The materials are mixed manually to obtain a homogeneous mixture. After that, some mixture is included in the injection. This is done to see the mixture passes through the nozzle. Most of the residual mixture is fed into a mold that can make five specimens in one experiment. The mold is coated with a lip moisturizer (as recommended by the dentist) before being used for printing. After inserting into the mold and trimming the edges, the mixture is allowed to stand for at least one hour before discharging as a specimen. This experiment was not subjected to temperature change at the time of the experiment. The temperature used in this experiment was room temperature.

Experiments were conducted to see the characteristics of the mixed material, whether the material can be homogeneously mixed, how the mixture is mixed, and whether the mixture can be passed through a nozzle (injection). In addition, it is also seen in the characteristics of specimens that have been made, i.e whether the specimen can be formed perfectly and how much compressive strength of each specimen.

After experiments and a hardened specimen were obtained, the specimen was left for 36 hours or more to make the hardening is more perfect. After 36 hours, the specimens are perfectly shaped to be tested for compression. The compression test was performed with the HT-2402 brand Hung Ta machine. Of the five specimens for each composition, 3 best specimens were selected for testing. Of the three tests, an average compressive strength score was taken.

RESULTS AND DISCUSSION

In many times, experiments were done to see the characteristics of a material which the material is capable of homogeneously mixing, texture owned by the material and the material capability continues in the passing nozzle when the percentage of hydroxyapatite (HA) mixture is increased. A nozzle is used in this experiment that is nozzle (hole) which owned by injection, where the material will be tried to pass nozzle 0.75 mm. If the mixture is difficult to pass through the nozzle, it will be tried on a 2 mm nozzle.

The first experiment was conducted based on research conducted by Samad & Jafaar (2009), the composition of PMMA: MMA = 1: 1 (w/w) with a percentage of HA mixture of 0%, 20%, 40%, and 60%. In a material mixed with 60% HA percentage, the mixture of this material does not mix homogeneously and it is still grained. Therefore, the mixture of this material is could not pass through the nozzle.

Figure 11. Specimens with PMMA composition: MMA = 1: 1 (w/w) with a percentage of HA 20%

The second experiment was based on a study conducted Samad & Jafaar (2009), the composition of PMMA: MMA = 0.75: 1 (w/w) with a percentage of 60% HA mixture. It is done to know the material can be mixed homogeneously or not with the reduction of PMMA powder material composition. As a result of this mixture, the material does not mix homogeneously and it is still grained. Therefore, the mixture of this material is could not pass through the nozzle.

Figure 12. Specimens with PMMA composition: MMA = 0.75: 1 (w/w) and a percentage of HA 60%

The third experiment was based on the composition of PMMA: MMA = 1: 5 (w/w) with a percentage of HA mixture of 0%, 20%, 40%, 60% and 80%. These materials mixtures have material characteristics, specimen conditions and different solidification times are on each material mixture. The difference can be seen in Table 1.

Table 1. Third Experimental Results

HA (%)	Mixed Characteristic	Specimen Condition	Solidification Time
0%	The mixture is reduced from 4 grams to ± 1.5 gram. It can pass 2mm nozzle.	Imperfect, transparent, elastic and bubbly	68 Hours
20%	The material is homogeneously mixed, but the residue undergoes evaporation. Able to pass 2mm nozzle.	Can be perfectly solid, white and milky pink	49 Hours 11 Minutes
40%	The mixture of the material is homogeneously mixed. When the material mixture is inserted into the injection, the liquid comes out first from the 2 mm nozzle and leaves a solid that can not come out of the 2 mm nozzle, this is like being squeezed. All specimens can be perfectly hardened, except for one incomplete specimen	All specimens can be perfectly hardened, an exception is one incomplete specimen	27 Hours 23 Minutes
60%	A mixture of materials capable of homogeneously mixed, powdery and white. Can not pass 2mm nozzle	Specimens can be solid, but fragile and white	21 Hours
80%	The material cannot be mixed homogeneously despite added citric acid, white powder texture. Giving citric acid has a function to make the mixture more slippery and able to pass nozzle to be smaller than 2 mm (Arora, 2013). Can not pass 2mm nozzle	-	-

Figure 13. Specimens with PMMA composition: MMA = 1: 5 (w/w) with a percentage HA of 40%

The fourth experiment was performed on a commercial composition ratio, the composition of PMMA: MMA = 2: 1 (w/v) with a percentage of 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, and 50%. These materials mixtures have material characteristics, different specimen conditions and solidification time on each material mixture. The difference can be seen in Table 2.

Figure 14. Specimens with composition PMMA : MMA = 2 : 1 (w/w) and percentage HA 10%

Four experiments are capable of passing 2 mm nozzle that will be compressive strength testing to determine the strength of specimens that have been formed from several previous compositions. The test results will be recorded in Table 3.

Table 2. Fourth Experimental Results

HA (%)	**Mixed Characteristic**	**Specimen Condition**	**Solidification Time**
0%	The mixture of the material is homogeneously mixed. Able to pass 2mm nozzle.	Perfectly solid and pink	23 Hours 41 Minutes
5%	The mixture of the material is homogeneously mixed. Able to pass 2mm nozzle.	Perfectly solid and pink	9 Hours 21 Minutes
10%	The mixture of the material is homogeneously mixed. Able to pass 2mm nozzle with more pressure, but a bit difficult because of the steam that prevents the suppressor.	Perfectly solid and rather white.	24 Hours
15%	The mixture of the material is homogeneously mixed. Can not pass 2mm nozzle.	Perfectly solid and rather white.	22 Hours 49 Minutes
20%	The mixture of the material is homogeneously mixed but the texture is powdered white. Can not pass 2mm nozzle.	Perfectly solid and rather white.	5 Hours 32 Minutes
25%	All materials can be mixed but the texture is powdered. A mixture can not pass nozzle2 mm.	Perfectly solid and pink rather white.	4 Hours 11 Minutes
30%	The mixture of the material is homogeneously mixed and powdered texture. Can not pass 2mm nozzle.	Perfectly solid and pink rather white.	9 Hours 25 Minutes
35%	The mixture of the material is homogeneously mixed and powdered texture. Can not pass 2mm nozzle.	Perfectly solid and pink rather white.	8 Hours 29 Minutes
40%	The mixture of the material is homogeneously mixed and powdered texture. Can not pass 2mm nozzle.	Perfectly solid and pink rather white.	7 Hours 21 Minutes
45%	The mixture of the material is homogeneously mixed and powdered texture. Can not pass 2mm nozzle.	Perfectly solid and pink rather white.	18 Hours 21 Minutes
50%	The mixture of the material is not homogeneously mixed, powdered white, and not stoichiometric.	-	-

Table 3. Results of *Compressive Strength*

PMMA : MMA	**HA%**	***Compressive Strength* (MPa)**	**Can Pass *Nozzle*?**
1 : 1	0%	22,32	Yes
1 : 1	20%	31,2	Yes
1 : 1	40%	6,76	Yes
0.2 : 1	40%	9,16	Yes
2 : 1	0%	21	Yes
2 : 1	5%	25,55	Yes
2 : 1	10%	25,62	Yes
2 : 1	15%	22,88	Yes
2 : 1	20%	24,05	No
2 : 1	25%	8,19	No
2 : 1	30%	18,08	No
2 : 1	35%	7,41	No
2 : 1	40%	14,75	No
2 : 1	45%	1,48	No
2 : 1	50%	3,29	No

Compositions that capable in passing nozzle will be formed to the following 15th graph based on the compressive strength of each mixture composition.

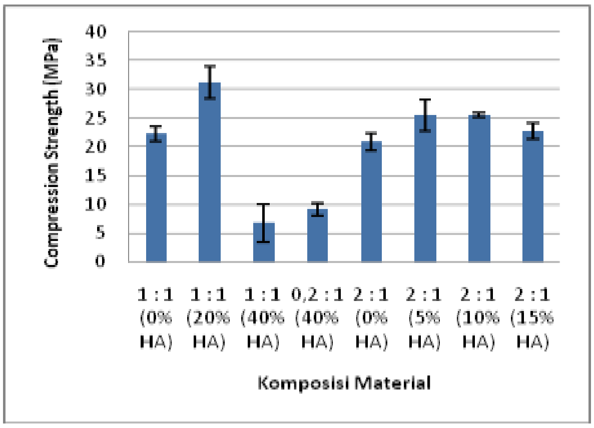

Figure 15. Compressive Strength *Graph*

From Fig. 15, it can be seen that the composition of PMMA: MMA is 1: 1 (w/w) with a 20% HA mixture having the highest graph among all compositions, but this mixture has a high standard deviation range. The second highest graph is seen in PMMA: MMA with a 2: 1 (w/v) composition and 10% HA mixture has a very small standard deviation range compared to other compositions. The third highest graph is seen in PMMA: MMA with a composition of 2: 1 (w/v) and 5% HA mixture, but it has a high standard deviation range. The fourth chart is shown in PMMA: MMA with a 2: 1 (w/v) composition and 15% HA mixture, but has a fairly high standard deviation range. The fifth highest graph is seen in PMMA: MMA with a 1: 1 (w/w) composition and a 0% HA mixture, but it has a fairly high standard deviation range. The sixth highest graph is seen in PMMA: MMA with a 2: 1 (w/v) composition and a 0% HA mixture, but it has a fairly high standard deviation range.

In Fig. 15, there are two pieces of the lowest graph owned by PMMA: MMA with a composition of 1: 5 (w/w) and a mixture of HA 40%, and PMMA: MMA with a 1: 1 (w/w) composition and 40% HA mixture. Between the two compositions are only on PMMA: MMA with a 1: 1 (w/w) composition and 40% HA mixture which has a very high standard deviation range. This means that the difference in the compressive strength of each specimen has a difference that is far or very large.

The composition obtained from the results of this study has a higher percentage of hydroxyapatite (HA) when compared with research conducted by Utami (2016). Whereas, the percentage of hydroxyapatite (HA) on specimens from the Utami (2016) contained only 5% of the total mixture.

When viewed from the time of solidification of the specimens produced, the study has a solidification time of 13 minutes to 36 hours until the specimen is fully hardened. This solidification time is longer than Tontowi *et al.* (2016) study which has a solidification time of 6 minutes. So this research material can be used to print the specimen with Portabee Kit machine.

CONCLUSION

Based on some experiments that have been done, it can be seen that the compositions cannot pass through the nozzle which has a diameter of 1.5 mm. The compositions may pass through a nozzle that having a diameter of 2 mm. In the composition of PMMA: MMA is 1: 1 (w/w) with a 20% HA mixture having the highest graph among all compositions. Therefore, this composition is chosen despite having a high standard deviation range. This composition is chosen because it has the highest percentage of HA present with the highest compressive strength value. However, as a second option, PMMA: MMA with a 2: 1 (w/v) composition and a 10% HA mixture is selected because it has the second highest graph and has a very small standard deviation range compared to the other compositions. Both of these compositions can be further investigated in the process of printing specimens with the Portabee Kit machine.

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REFERENCES

Ali, U., Karim, K.J., and Buang, N.A. (2015). A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA). *Journal of Polymer Reviews. 55*(4), 678-705. http://dx.doi.org/10.1080/15583724.2015.1031377

Boskey A.L. (2013). Bone Composition: Relationship to Bone Fragility and Antiosteoporotic Drug Effects. *BoneKEy Reports. 2*(447), 1-11. http://dx.doi.org/10.1038/bonekey.2013.181

Hosseinzadeh H.R.S., Emami, M., Lahiji, F., Shahi, A.S., Masoudi, A., and Emami, S. (2013). *The Acrylic Bone Cement in Arthroplasty*. In: Arthroplasty – Update. 101–128. http://dx.doi.org/10.5772/53252

Puska, M., Aho, A.J., and Vallittu, P. (2011). *Polymer Composites for Bone Reconstruction*. In: Advances in Composite Materials - Analysis of Natural and Man-Made Materials. 55-72.

Rashamadi, S., Hasanzadeh, R. and Mosalman, S. (2017). Improving the Mechanical Properties of Poly Methyl Methacrylate Nanocomposites for Dentistry Applications Reinforced with Different Nanoparticles. *Journal of Polymer-Plastics Technology and Engineering. 56*(16), 1730-1740. http://dx.doi.org/10.1080/03602559.2017.1289402

Roeder, R.K., Converse, G.L., Kane, R.J., and Yue, W. (2008). Hydroxyapatite-Reinforced Polymer Biocomposites for Synthetic Bone Substitutes. *Journal of Materials*. *60*(3), 38-45. http://dx.doi.org/10.1007/s11837-008-0030-2

Samad, H.A. and Jaafar, M. (2009). Effect of Polymethyl Methacrylate (PMMA) Powder to Liquid Monomer (P/L) Ratio and Powder Molecular Weight on the Properties of PMMA Cement. *Journal of Polymer-Plastics Technology and Engineering. 48*(5), 554-560. http://dx.doi.org/10.1080/03602550902824374

Tontowi, A.E., Kuswanto, D., Sihaloho, R.I., and Sosiati, H. (2016). Composite of [HA/PMMA] for 3D-Printer Material Application. *AIP Conference Proceedings. 1755*(1), 150020. http://dx.doi.org/10.1063/1.4958593

Utami, P. (2016). Optimasi Parameter Proses Ekstrusi Pasta Biokomposit [PMMA/Hidroksiapatit/ Serisin] Pada Mesin Printer 3D Menggunakan Metode Response Surface. *Skripsi*. Universitas Gadjah Mada.

Zebarjad S.M., Sajjadi, S.A., Sdrabadi, T.E., Yaghmaei, A., and Naderi, B. (2011). A Study on Mechanical Properties of PMMA/Hydroxyapatite Nanocomposite. *Engineering*. *3*, 795-801. http://dx.doi.org/10.4236/eng.2011.38096